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Polysaccharide**

Journal:	<i>Physical Chemistry Chemical Physics</i>
Manuscript ID:	CP-ART-04-2012-041183.R1
Article Type:	Paper
Date Submitted by the Author:	n/a
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# Temperature Dependence of Thermal Diffusion for Aqueous Solutions of Monosaccharide, Oligosaccharide, and Polysaccharide

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Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

We studied the thermal diffusion behavior for binary aqueous solutions of glucose, maltotriose, maltohexaose, pullulan, and dextran by means of thermal diffusion forced Rayleigh scattering (TDFRS). The investigated saccharides with molar masses between 0.180 and 440 kg/mol were studied in the temperature range between 15 and 55°C. The thermal diffusion coefficient  $D_T$  and the Soret coefficient  $S_T$  of all solutions increase with increasing temperature. For maltohexaose and the polymers the thermal diffusion coefficient changes sign from negative to positive with increasing temperature, whereas glucose and maltotriose show only positive values in the entire investigated temperature range. While we were able to find a master curve to describe the temperature dependence of  $D_T$ , we were no able to find a similar expression for  $S_T$ . This comprehensive study allows for the first time the determination of the interaction parameters for the polymer and the solvent within the theoretical framework suggested by Würger [*Phys. Rev. Lett.*, 2009, **102**, 078302].

## 1 Introduction

The diffusion of fluid mixtures has been studied extensively by experiments, theories, and computer simulations.<sup>1,2</sup> For a binary system under isothermal condition, the diffusion of the solute molecules can be driven by a composition gradient well-known as Fick's law. Brownian motion is the origin of the fluctuation of molecules which results in the diffusion of solute molecules. The diffusion coefficient of a polymer in solution is usually determined by dynamic light scattering<sup>3</sup> and is related to the friction of the solute by the Stokes-Einstein relationship as

$$D(T) = \frac{k_B T}{6\pi\eta r}, \quad (1)$$

where  $r$  is the radius of the solute and  $\eta$  is the solvent viscosity. In the case of polymers the hydrodynamic radius  $R_h$  is used instead of  $r$ .<sup>4</sup> This equation indicates the temperature dependence of the diffusion coefficient  $D(T)$  relates to the product of the temperature  $T$  and the temperature dependence of the viscosity  $\eta(T)$ . On the other hand the diffusion coefficient  $D$  of polymers is related to the number of monomers  $N$  by  $D \propto N^{-\nu}$  where the exponent  $\nu$  depends on the chain expansion due to segment-solvent interactions.

For mixtures subjected to a temperature gradient at a constant pressure, one observes a diffusion current of the solute as a nonisothermal effect.<sup>5</sup> This is known as thermal diffusion or Ludwig-Soret effect which leads to the formation of a concentration gradient.<sup>6–8</sup> In the case of a binary mixture, the flux of the solute  $\mathbf{J}$  is phenomenologically described by the sum of two driving forces  $\nabla w$  and  $\nabla T$  as<sup>5</sup>

$$\mathbf{J} = -\rho D \nabla w - \rho w(1-w) D_T \nabla T. \quad (2)$$

Here,  $w$  and  $\rho$  denote the solute weight fraction and the density of the solution, respectively.  $D$  and  $D_T$  are the mutual diffusion coefficient and the thermal diffusion coefficient, respectively. In a steady state where the mass flow vanishes ( $\mathbf{J}=0$ ), the concentration gradient is given by

$$\nabla w = -S_T w(1-w) \nabla T. \quad (3)$$

Here,  $S_T (= D_T/D)$  is the Soret coefficient. The sign of the Soret coefficient indicates the direction of the flux of the solute. The positive sign of  $S_T$  means that the solute migrates to the cold side.<sup>9</sup> In general for organic solutions of polymers, the polymers move to the cold side due to their heavier mass and larger size in comparison with the solvent molecules.<sup>10–13</sup>

Due to the difficulty of nonisothermal condition, there are fewer experimental studies on the thermal diffusion coefficient  $D_T$  and the Soret coefficient  $S_T$  compared to measurements of the mutual diffusion coefficient  $D$ . Especially, for aqueous solutions of biopolymers the number of publications is small, although the contributions of the Ludwig-Soret effect

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to biological processes are of general interest. Recently, the Ludwig-Soret effect of DNAs, proteins, and polysaccharides has been studied systematically.<sup>14–19</sup> One of the characteristics of the biopolymers is a sign inversion of  $D_T$  and  $S_T$  as a function of temperature.<sup>19</sup> Typically, the sign of  $D_T$  and  $S_T$  is negative at lower temperatures, and the sign changes from negative to positive with increasing temperature. The negative sign means the polymers migrate to the hot side of the fluid. Only for the water soluble poly(*N*-isopropylacrylamide) [PNIPAM] in alcohols has a negative slope of  $S_T(T)$  and  $D_T(T)$  with temperature has been found. For these systems a sign inversion from positive to negative with increasing temperature is observed,<sup>20,21</sup> while the Soret coefficient of PNIPAM in water is always positive.<sup>22</sup> Piazza and co-authors suggested an empirical equation as follows<sup>14,23,24</sup>

$$S_T(T) = S_T^\infty \left[ 1 - \exp\left(\frac{T_{\text{inv}} - T}{T_0}\right) \right] \quad (4)$$

to describe the temperature dependence of  $S_T$ . Here,  $S_T^\infty$  represents a saturation value of  $S_T$  at high temperature,  $T_{\text{inv}}$  is the temperature where  $S_T$  changes the sign, and  $T_0$  indicates the strength of temperature effects. This rather universal behavior holds for various systems not only for colloidal suspensions but also for water soluble polymers<sup>19</sup>. Recently, Piazza and co-authors reported a scaled temperature dependence of  $S_T$  for colloidal systems as follows,<sup>25</sup>

$$\frac{S_T(\tilde{T})}{S_T^\infty} = 1 - \exp[A(1 - \tilde{T})]. \quad (5)$$

Here,  $\tilde{T}$  is defined as  $\tilde{T} = T/T_{\text{inv}}$  and  $A$  is a dimensionless parameter as  $A = T_{\text{inv}}/T_0$ . Although the physical meaning of the parameter  $A$  is still an open question, it is considered that the equation describes a universal behavior of the temperature dependence of  $S_T$  for colloidal systems. It is of great interest to study whether the same scaling behavior holds also for other systems. Thus, the first aim of this contribution is to study the temperature dependence of the Soret coefficient for binary systems composed of mono-, oligo-, and polysaccharides as solute in water and to extend the recent studies by Blanco et al.<sup>26,27</sup>

Further we study the temperature dependence of the Soret coefficient  $S_T$ ,<sup>22,28–31</sup> and the thermal diffusion coefficient  $D_T$  to compare it with other aqueous systems. Experimental data show an increasing  $D_T$  with increasing temperature for biopolymers and water-soluble synthetic polymers.<sup>19</sup> The slope of  $D_T$  versus temperature seems to be linear, although the slope and the sign inversion temperature depend on the systems.

Another purpose of the paper is to study the thermal diffusion as function of the molecular weight at different temperatures. We cover a molecular weight range from the monomer

with 0.180 kg/mol up to polymers with 440 kg/mol. Recently, Stadelmaier and Köhler reported a crossover behavior of the Ludwig-Soret effect for systems of polystyrene [PS] in various solvents as function of molecular weight.<sup>32</sup> They revealed that  $D_T$  is scaled by the solvent viscosity  $\eta$ , and  $\eta D_T$  does not depend on the molecular weight nor on the solvent quality in the molecular weight range of PS chains longer than the Kuhn segment length, whereas it depends on the solvent for shorter chains. This crossover behavior is predicted by the simulation work of Zhang and Müller-Plathe.<sup>33</sup> The simulation work was supported by an experimental study of very flexible glycols in ethanol, where  $D_T$  reaches already a constant value after 2 repeating units.<sup>34</sup>

Recently, Würger studied the molecular weight dependence of the thermal diffusion behavior theoretically.<sup>35,36</sup> He finds that the thermal diffusion coefficient depends on the radius of gyration  $R_G$  given by the scaling law  $R = \ell \cdot N^\nu = \mu \cdot M^\nu$ , with the degree of polymerization  $N$  and the scaling exponent  $\nu$ , the radius  $a$  of the single bead (monomer), the dynamic viscosity  $\eta$ , a numerical constant  $\kappa$ , the thermal expansion coefficient  $\beta = -(1/c) \cdot dc/dT$  and the energies  $\epsilon_p$  and  $\epsilon_s$  of the bead forming the polymer and the solvent, respectively.

$$\frac{D_T}{D_T^{\text{max}}} = 1 - \frac{\psi}{M^\nu} \quad (6)$$

with

$$\psi = \left[ \frac{\epsilon_s}{\epsilon_p} + \frac{(\epsilon_s - \epsilon_p)}{(\beta \epsilon_p T)} \right] \frac{6\pi a}{\kappa \mu} \quad (7)$$

He showed that the balance of the interactions between segment and solvent can give rise to a negative thermal diffusion coefficient in the low molecular weight regime, whereas for high molecular weights the thermal diffusion coefficient is independent of the molecular weight. When the interaction potential of the solvent  $\epsilon_s$  is larger than that of the solute  $\epsilon_p$ , a negative  $D_T$  is observed in the low molecular weight regime. This theory describes the experimental results of PS solutions well<sup>32,37</sup>, where it is shown that the long-range hydrodynamic interactions dominate the Brownian diffusion, while they are not important for thermal diffusion. This last point is in contradiction to the results for colloids, where hydrodynamic interactions are important for both diffusion processes.<sup>38,39</sup> It is interesting to investigate, whether Würger's results hold also for polar polymers such as the aqueous polymer solutions which have a negative thermal diffusion coefficient.

In this report the Ludwig-Soret effect of binary aqueous solutions of monosaccharide, oligosaccharide, and polysaccharide was studied by means of thermal diffusion forced Rayleigh scattering (TDFRS) as a function of temperature. The monosaccharide used in this study is D-glucose (Glc,  $M=180.2 \text{ g mol}^{-1}$ ). Here, glucose is the basic constituent for all other samples. As oligosaccharides, maltotriose and maltotetraose are used. Maltotriose is composed of  $\alpha$ -D-(1 $\rightarrow$ 4)-

linked glucose [Glc( $\alpha$  1-4)Glc( $\alpha$  1-4)Glc,  $M=504.4 \text{ g mol}^{-1}$ ]. Maltotriose is also composed of  $\alpha$ -D-(1 $\rightarrow$ 4)-linked glucose [Glc( $\alpha$  1-4)Glc( $\alpha$  1-4)Glc( $\alpha$  1-4)Glc( $\alpha$  1-4)Glc,  $M=990.9 \text{ g mol}^{-1}$ ]. The polysaccharides are pullulan and dextran which have been well characterized in water.<sup>40–42</sup> Pullulan is composed of  $\alpha$ -D-(1 $\rightarrow$ 6) linked maltotriose. Dextran is composed of  $\alpha$ -D-(1 $\rightarrow$ 6)-linked glucose with some short  $\alpha$ -D-(1 $\rightarrow$ 3)-linked glucose branching units. It is considered that the series of these saccharides is a good choice to study the Ludwig-Soret effect in regard to the molecular weight dependence from the monomer to high molecular weight polymers, because the regularity of the glycosidic bonds of solutes is changed in a systematic manner.

## 2 Experimental

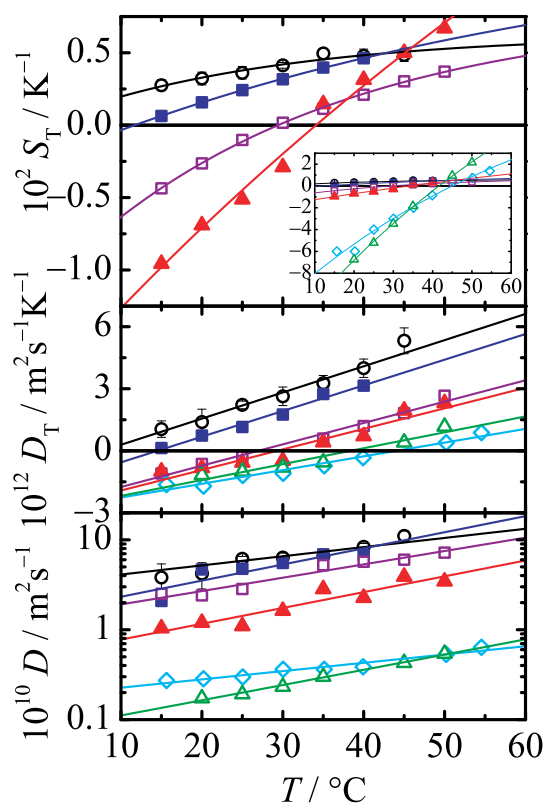
**Materials.** Glucose, maltotriose, and maltotriose were purchased from Wako Chemical and are used as received. Pullulan (Hayashibara Co.) was purified three times by a methanol precipitation from aqueous solution and dextran (Polymer Standard Service) was also purified.<sup>43</sup> The weight averaged molecular weights shown in this report for pullulan are 4.2 and 440  $\text{kg mol}^{-1}$  and for dextran is 86.7  $\text{kg mol}^{-1}$ .<sup>18,19</sup> Distilled and deionized water (milli-Q) was used as solvent. For TDFRS measurements a small amount of the dye, Basantol Gelb (BASF), was used to create the temperature gradient.<sup>44</sup> The concentration of the aqueous solutions of monosaccharide, oligosaccharides and pullulan(4k) was 10.0  $\text{g L}^{-1}$ . The data of dextran and pullulan(440k) included from previous publications were measured at the concentration of 5.0  $\text{g L}^{-1}$ .<sup>18,19</sup>

**Methods.** The Soret coefficient  $S_T$ , the thermal diffusion coefficient  $D_T$ , and the mutual diffusion coefficient  $D$  are obtained by the thermal diffusion forced Rayleigh scattering (TDFRS) method. The details of the TDFRS have been described elsewhere.<sup>45,46</sup> The TDFRS measurements were carried out in a temperature range from 15 to 55°C. The temperature of the sample cell was controlled by circulating water from a thermostat bath with an uncertainty of 0.02°C. The sample solutions were filtered directly into the optical quartz cell with 0.2 mm path length (Hellma) through 0.22  $\mu\text{m}$  membrane filter (Millipore).

The normalized heterodyne signal intensity of TDFRS experiments,  $\zeta_{\text{het}}(t)$ , to the thermal signal is related to the Soret coefficient  $S_T$  and mutual diffusion coefficient  $D$  as follows:

$$\zeta_{\text{het}}(t) = 1 + \left( \frac{\partial n}{\partial T} \right)_{p,w}^{-1} \left( \frac{\partial n}{\partial w} \right)_{p,T} S_T w (1-w) [1 - \exp(-Dq^2t)] \quad (8)$$

Here,  $t$  is the time,  $n$  the index of refraction,  $q$  the scattering vector,  $(\partial n / \partial T)_{p,w}$  and  $(\partial n / \partial w)_{p,T}$  are the refractive index increments with temperature and weight fraction.  $(\partial n / \partial T)_{p,w}$



**Fig. 1** (Color online) Soret coefficient  $S_T$ , thermal diffusion coefficient  $D_T$ , and mutual diffusion coefficient  $D$  for aqueous solutions of glucose( $\circ$ ), maltotriose ( $\blacksquare$ -blue), maltotriose ( $\square$ -purple), pullulan-4k ( $\blacktriangle$ -red), dextran ( $\diamond$ -cyan)<sup>18</sup>, and pullulan-440k ( $\triangle$ -olive)<sup>19</sup>. The curves in  $S_T$  are fitted one using Eq. 4, and in  $D_T$  and  $D$  the lines are obtained with linear regression.  $S_T$  of dextran and pullulan(440k) is only shown in the inset.

and  $(\partial n / \partial w)_{p,T}$  must be determined separately. A scanning Michelson interferometer operating at a wavelength of 632.8 nm is used.<sup>47</sup>

## 3 Results and discussion

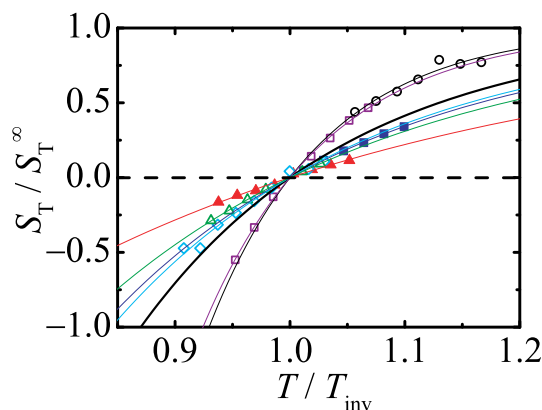
Figure 1 shows the Soret coefficient  $S_T$ , the thermal diffusion coefficient  $D_T$ , and the mutual diffusion coefficient  $D$ , as function of temperature, for 10.0  $\text{g L}^{-1}$  aqueous solutions of glucose, maltotriose, maltotriose, and pullulan(4k), and for 5.0  $\text{g L}^{-1}$  aqueous solutions of dextran and pullulan(440k). Earlier studies<sup>18,19</sup> showed that the concentration effect on the thermal diffusion behavior is small in this concentration range, so that the experimental results for the different concentrations can be compared. The curves in the plot of  $S_T$  are obtained by a nonlinear least-square fit using Eq. 4, and the lines in the plot of  $D_T$  and  $D$  are obtained by linear regression, which at first glance seem to describe the data sufficiently

well. Later we will see that a non-linear equation to describe the temperature dependence of  $D_T$  similar to Eq. 4 gives more consistent results. The obtained parameters  $T_{\text{inv}}$ ,  $S_T^\infty$ , and  $T_0$  in Eq. 4 are summarized in Table 1. All samples show an increase of  $S_T$ ,  $D_T$ , and  $D$  with increasing temperature.  $S_T$  and  $D_T$  of glucose and maltotriose in water have a positive sign in the investigated temperature range, though it is expected that the sign change takes place at lower temperatures. For all other systems  $S_T$  and  $D_T$  change their sign from negative to positive with increasing temperature in the investigated temperature range. The sign change temperature increases with increasing the molecular weight of saccharides. The magnitude and the slope of  $S_T$  for polymers are apparently larger than that of glucose and oligosaccharides. Contrary, the magnitude and the slope of  $D_T$  for polymers become smaller with increasing the molecular weight. The diffusion coefficient  $D$  increases linearly on the semi-logarithmic plot with increasing temperature for all samples in the investigated temperature. The plots of  $D$  as function of the inverse of absolute temperature (Arrhenius plot, data not shown) show linear lines for all of samples with the activation energies between  $17 \text{ kJ mol}^{-1}$  and  $31 \text{ kJ mol}^{-1}$ .<sup>19</sup> Here, the activation energy shows no apparent correlation with the molecular weight because the activation energy might also depend on branching effects and other conformational changes between the monomer, oligomer and polymer. On the other hand, the temperature dependence of the thermal diffusion coefficient  $D_T$  clearly shows that the slope decreases with increasing molecular weight as shown in Fig. 1. The temperature and the molecular weight effect will be discussed in detail below.

### 3.1 Temperature effect for Soret coefficient

The results of the temperature dependence of the Soret coefficient  $S_T(T)$  were described well by Eq. 4 for all samples as shown in Fig. 1. The saturation value of  $S_T^\infty$  and the sign inversion temperature  $T_{\text{inv}}$  tend to have larger magnitudes for solute molecules with a larger molecular weight. Recently, Vigolo et al. reported the temperature dependence of  $S_T(T)$  for the systems of SDS micelles in NaCl and NaOH aqueous solutions.<sup>25</sup> They revealed that the scaled Soret coefficient  $S_T(\tilde{T})/S_T^\infty$  lies nicely on a single master curve when the  $S_T(\tilde{T})/S_T^\infty$  is plotted against the normalized temperature  $\tilde{T} (= T/T_{\text{inv}})$ . The master curve is described by the function of Eq. 5. We follow the same route investigating the temperature dependence of  $S_T(\tilde{T})/S_T^\infty$  for the binary systems of saccharide in water.

Figure 2 shows the  $S_T(\tilde{T})/S_T^\infty$  as a function of  $\tilde{T}$  for all saccharide solutions. The bold curve is obtained by a nonlinear least-square fit with Eq. 5 using all data points and the parameter  $A (= T_{\text{inv}}/T_0)$  in Eq. 5 was obtained as  $A = 5.5 \pm 0.4$ . Here,  $\pm$  denotes one standard deviation. The thinner curves

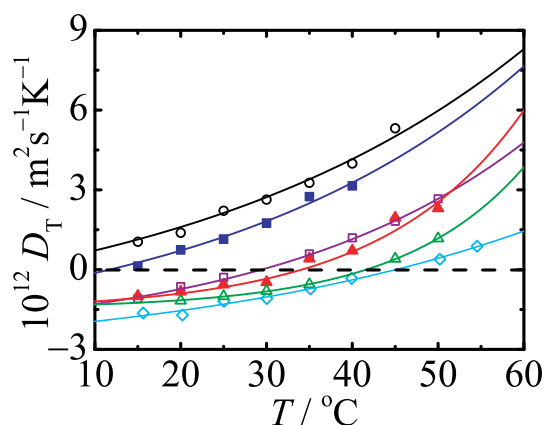


**Fig. 2** The normalized Soret coefficient  $S_T(\tilde{T})/S_T^\infty$  as a function of  $T/T_{\text{inv}}$ . The solid curve is obtained by a fitting using Eq. 5 for all data points. Symbols have the same meaning as in Fig. 1.

are obtained for each sample. The obtained parameter  $A$  is summarized in Table 1. The result indicates that there is no clear master curve for all saccharide solutions. In the case of the SDS micelle systems, the dimensionless parameter  $A$  was reported as  $A \simeq 16$  where the Soret coefficients of SDS micelles are scaled well in the presence and absence of salt. For a suspension of *fd*-virus  $A = 15$  and  $6.6$  had been found, depending on the concentration.<sup>48</sup> In this study for aqueous solutions of saccharides with a broad molecular weight range we do not find a master curve to describe the temperature dependence of the normalized Soret coefficients. One of the reasons is that scaling concepts for the diffusion coefficient hold only for the polymer range and fail in the oligomer and monomer range. Additionally the temperature variation of molecular interactions between solute and solvents needs to be taken into account.

### 3.2 Temperature influence on thermal diffusion coefficient

The thermal diffusion coefficient  $D_T$  increases linearly with increasing temperature for all samples (c.f. Fig. 1) and the sign inversion temperature of  $D_T$  must be identical with the sign inversion temperature  $T_{\text{inv}}$  of  $S_T$  because of the definition of  $S_T = D_T/D$ . However, it is found that the sign inversion temperatures determined using  $S_T$  with Eq. 4 do not agree with the sign inversion temperature using a linear regression to describe the temperature dependence of  $D_T$ . The deviations become larger with increasing molecular weight of the samples. This result indicates that the temperature dependence of  $D_T(T)$  is nonlinear. One possible attempt would be to combine the theoretical description of the diffusion coefficient by Eyring and combine it with the empirical approach by Piazza, but this would lead to a sum of two exponentials and four



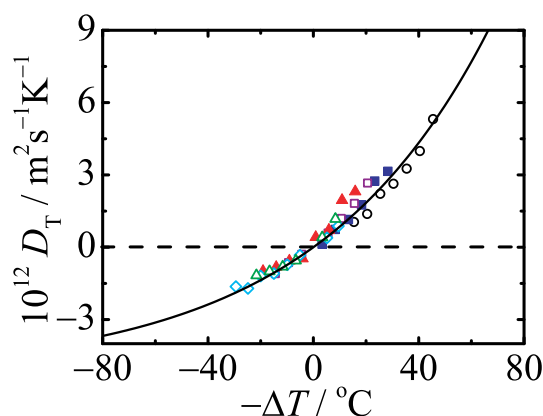
**Fig. 3** Thermal diffusion coefficient  $D_T$  as function of temperature  $T$ . Here, the curves are obtained by a fitting using Eq. 9. Symbols have the same meaning as in Fig. 1.

adjustable parameters, which can not be determined reliably. Therefore, we express  $D_T(T)$  by the following equation,

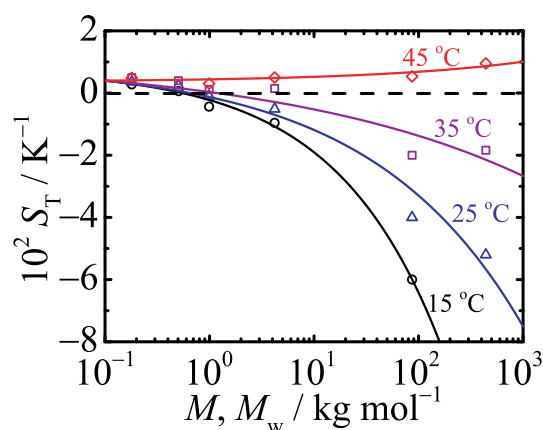
$$D_T(T) = D_{T0} \left[ 1 - \exp\left(\frac{\Delta T}{T_1}\right) \right]. \quad (9)$$

Here,  $D_{T0}$  represents the minimum  $D_T$  value,  $T_1$  is an indicator of the strength of the temperature effect and  $\Delta T = T_{\text{inv}} - T$  is the distance to the sign inversion temperature  $T_{\text{inv}}$  also determined from the temperature dependence of the Soret coefficient. This equation for  $D_T(T)$  has the same form as Eq. 4. Figure 3 shows the  $D_T(T)$  as a function of temperature with the fitted curves which are obtained by a nonlinear least-square fit using Eq. 9. Here, we fixed  $T_{\text{inv}}$  to the value obtained for the Soret coefficient and treated  $D_{T0}$  and  $T_1$  as adjustable parameters. The obtained values are summarized in Table 1.

The temperature dependence of  $D_T$  is described well by the fitting curve. To study the temperature effect on  $D_T$  in more detail, we plotted  $D_T(T)$  as a function of  $\Delta T$  ( $=T_{\text{inv}} - T$ ) as shown in Fig. 4. It is found that all  $D_T$  values fall on a single master curve. The solid curve in Fig. 4 is obtained by a nonlinear least-square fit to all data points using Eq. 9. The parameters  $D_{T0}$  and  $T_1$  are obtained as  $D_{T0} = (-4.78 \pm 0.91) \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$  and  $T_1 = 59.8 \pm 9.2 \text{ K}$ , respectively. In contrast to the Soret coefficient the mass or the size effect cancels out, so that we find a single master curve for  $D_T$  for all investigated saccharides when it is plotted against  $\Delta T$ . The result indicates that the curvature of  $D_T$  against temperature is not affected by the mass and the size of solute molecules, although the temperature dependence of  $S_T$  is apparently associated with the size and the mass of the solutes.



**Fig. 4** Thermal diffusion coefficient  $D_T$  as function of temperature difference  $\Delta T$  for all saccharide solutions. Symbols have the same meaning as in Fig. 1. The curve is obtained by a nonlinear least-square fit according to Eq. 9.



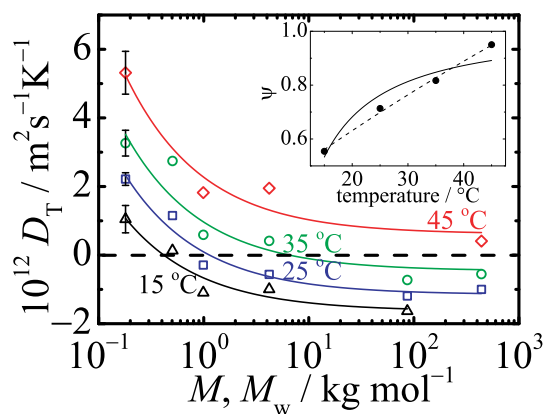
**Fig. 5** Molecular weight dependence of Soret coefficient  $S_T$  obtained at 15, 25, 35, and 45 °C. Curves are drawn to guide the eye.

### 3.3 Molecular weight dependence

The molecular weight dependence of the Soret coefficients  $S_T$  at the selected temperatures of 15, 25, 35, and 45 °C are shown in Fig. 5. The sign inversion of  $S_T$  from positive to negative shifts towards lower temperatures with increasing molecular weight. The magnitude of the negative  $S_T$  value becomes larger with increasing molecular weight, which is mainly due to the consequence of  $S_T = D_T/D$  where  $D$  has the form of  $D \propto N^{-\nu}$ . The lines in Fig. 5 are guides to the eye, because there is no theoretical expression available which describes the molecular weight dependence of the Soret coefficient  $S_T$ .

In contrast we can use Eq. 6 to describe the molecular weight dependence of the thermal diffusion coefficients  $D_T$  at the selected temperature 15, 25, 35, and 45 °C as a function of molecular weight as shown in Fig. 6. The resulting  $\psi$ -parameters as function of temperature are shown in the in-

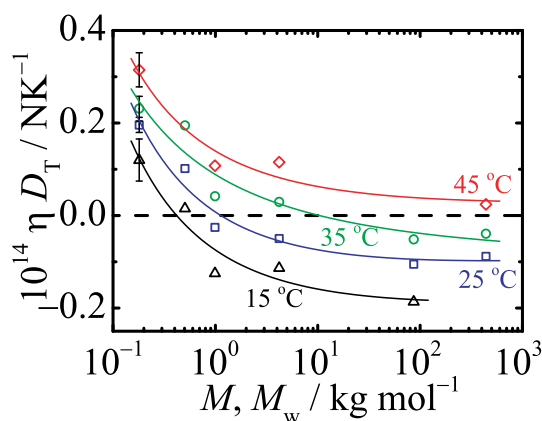




**Fig. 6** Molecular weight dependence of thermal diffusion coefficient  $D_T$  at 15, 25, 35, and 45 °C. Lines are fits according to Eq. 6. The inset shows the determined  $\psi$ -parameter as function of temperature. The dashed line is a fit with an adjustable thermal expansion coefficient  $\beta$ , while the solid line describes a fit with the experimentally determined  $\beta$ -values for water.

set of Fig. 6. Beside some numerical constants  $\psi$  (c.f. Eq. 7) depends on the thermal expansion coefficient  $\beta$ , the energies  $\varepsilon_p, \varepsilon_s$  of the polymer bead and the solvent, respectively. The dashed line is a fit with an adjustable thermal expansion coefficient  $\beta$ , while the solid line represents a fit, where  $\beta$  has been fixed to the experimentally observed thermal expansion coefficient of water<sup>49</sup>. It needs to be pointed out that the energy ratio of  $\varepsilon_s/\varepsilon_p$  changes only slightly from 0.96 to 0.97 depending on an adjustable or fixed  $\beta$ , respectively. In the case of the organic mixtures the ratio of  $\varepsilon_s/\varepsilon_p$  is larger than 1, resulting in an increasing thermal diffusion coefficient. It would be desirable to have also temperature and molecular weight dependent studies for organic polymers to regard the ratio of the interaction energies in this case. It is expected that the temperature is less pronounced compared to the polar systems.

So far there are only a few molecular weight dependent studies for aqueous systems.<sup>27,34,50</sup> The studies of aqueous saccharide solutions are limited to the oligomer range and have not been analyzed in detail. On the other hand, for non-polar polymers in organic solvents the molecular weight dependence of the thermal diffusion coefficient has been studied in a number of publications.<sup>12,33,37,51</sup> For PS in various solvents the thermal diffusion coefficient is independent of the molecular weight in the high mass regime, where the sign of the thermal diffusion coefficient is positive.<sup>32,37</sup> The thermal diffusion coefficient scales with the inverse of the viscosity and the value of  $\eta D_T$  is constant in the high molecular mass regime and even independent of the solvent. On the other hand, it decreases approaching the oligomer and monomer range, and sometimes even shows negative values in some solvents. The molecular weight dependence of the PS solutions



**Fig. 7** Molecular weight dependence of thermal diffusion coefficient normalized by the inverse of viscosity  $\eta D_T$  at 15, 25, 35, and 45 °C. Curves are fitted results according to Eq. 6.

is inverted compared to this study for saccharides in water, where the sign of the thermal diffusion coefficient of saccharides is negative in the high mass regime and becomes more positive with decreasing molecular mass as shown in Fig. 7. Here, the water viscosity is used to calculate  $\eta D_T$  and the figure shows that  $\eta D_T$  depends apparently on temperature, which has not been investigated for organic polymers. It might be interesting to notice that  $\eta D_T$  has a dimension as force per temperature. The negative sign of  $D_T$  at high molecular weight can be explained qualitatively by the expression of Würger with a ratio of  $\varepsilon_s/\varepsilon_p$  smaller than one. But here further temperature and concentration dependent studies are necessary to gain a better understanding of the thermal diffusion behavior of aqueous solutions.

In aqueous solutions, especially at low temperatures, interactions via hydrogen bonds dominate the thermal diffusion behavior. At higher temperatures the strength of hydrogen bonds in the system is weakened, so that entropic contributions become more important which leads often to an ordinal behavior of the thermal diffusion, i.e., positive sign of  $S_T$  and  $D_T$ . As has been shown the impact of hydrogen bonds on the thermal diffusion behavior can not only be weakened by increasing the temperature, but also by adding a component like urea, which weakens the hydrogen bonds of the water soluble polymer.<sup>19</sup> As shown in Figs. 6 and 7 the thermal diffusion behavior changes sign with increasing molecular weight, which could be reproduced by the theoretical approach of Würger by modifying the ratio of interaction energies of the segments and the solvents. In general negative Soret coefficients are found under a poor solvent conditions.<sup>34,52,53</sup> Here, the solubility of the solute molecules plays an important role. While for instance glycol has a positive Soret coefficient in ethanol, negative  $S_T$ -values are observed for diglycol and triglycol in ethanol and higher glycol oligomers are not soluble at all. The

solution of pullulan in DMSO, where DMSO is polar and an aprotic solvent, shows only positive values of  $D_T$  and  $S_T$ .<sup>19</sup> So that we assume at least two key roles; the effects of hydrogen bonds network and of a low solubility, which can lead to negative Soret and thermal diffusion coefficient at lower temperatures and high molar masses in aqueous saccharide solutions.

## 4 Conclusions

For the binary systems of mono-, oligo-, and poly- saccharide in water, the temperature dependences of the Soret coefficient  $S_T$  and the thermal diffusion coefficient  $D_T$  have been studied. The sign inversion behavior of the Soret coefficient  $S_T(T)$  lies not on a master curve proposed by Piazza and coauthors as  $S_T(\tilde{T})/S_T^\infty$  vs.  $\tilde{T} = T/T_{\text{inv}}$ . Contrary, the temperature dependence of the thermal diffusion coefficient  $D_T(T)$  falls on a single curve on the plot of  $D_T(T)$  vs.  $\Delta T = T_{\text{inv}} - T$ . Moreover, it is found that the temperature dependence of  $D_T(T)$  is nonlinear in the investigated temperature range. The plots of molecular weight dependence show that the  $D_T$  tends to saturate at a negative value for high molecular weight polymers, whereas it increases with lowering the molecular weight and changes the sign from negative to positive. The molecular weight dependence is upside down compared to the observed behavior for PS solutions, but it agrees with findings for aqueous solutions of water.<sup>34</sup> The molecular weight dependence of  $D_T$  can be described by a theoretical model by Würger, whereas the ratio of the interaction energies  $\varepsilon_s/\varepsilon_p$  smaller than one, while in the same model leads to a ratio larger than one for PS systems. This discrepancy between PS systems and aqueous saccharide solutions may be attributed to the effect of the interactions through hydrogen bonds, where the hydrogen bonds network in the system play a significant role for the thermal diffusion. To understand the molecular mechanism of this behavior, the temperature dependence of the segment-solvent interactions on their thermodynamic quantities needs to be taken into account.

**Acknowledgments** The authors are indebted to Jan Dhont for his kind help and to Gerhard Meier for correction reading. The technical support of Hartmut Kriegs is appreciated. The sample donation by Hayashibara co. is acknowledged. This work is partially supported by Deutsche Forschungsgemeinschaft (grant Wi 1684) and by the Ministry of Education, Science, Sports and Culture, Japan (Grant-in-Aid for Scientific Research).

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**Table 1** The values of  $T_{\text{inv}}$ ,  $S_{\text{T}}^{\infty}$ , and  $T_0$  obtained with Eq. 4 and  $A$  obtained by Eq. 5 for mono-, oligo-, and poly- saccharides in water. Also the values of  $D_{\text{T}0}$  and  $T_1$  obtained with Eq. 9, where  $T_{\text{inv}}$  is the value obtained from  $S_{\text{T}}$  with Eq. 4 for mono-, oligo-, and poly- saccharides in water. Here,  $\pm$  means one standard deviation.

Solute	Soret coefficient				Thermal diffusion coefficient	
	$T_{\text{inv}}$ / $^{\circ}\text{C}$	$S_{\text{T}}^{\infty}$ / $\text{K}^{-1}$	$T_0$ / $\text{K}$	$A$	$10^{12} D_{\text{T}0}$ / $\text{m}^2\text{s}^{-1}\text{K}^{-1}$	$T_1$ / $\text{K}$
glucose	$-0.4 \pm 7.7$	$0.006 \pm 0.002$	$27.7 \pm 22.2$	$9.9 \pm 0.3$	$-2.51 \pm 0.64$	$-41.4 \pm 7.1$
maltotriose	$11.7 \pm 0.3$	$0.014 \pm 0.002$	$67.8 \pm 12.5$	$4.2 \pm 0.1$	$-2.85 \pm 1.55$	$-37.1 \pm 14.7$
maltohexaose	$29.4 \pm 0.2$	$0.008 \pm 0.001$	$33.1 \pm 2.5$	$9.2 \pm 0.1$	$-2.73 \pm 0.35$	$-30.2 \pm 3.0$
pullulan(4k)	$34.1 \pm 0.8$	$0.058 \pm 0.069$	$123 \pm 145$	$2.5 \pm 0.1$	$-1.55 \pm 0.44$	$-16.4 \pm 3.4$
dextran	$45.0 \pm 1.1$	$0.127 \pm 0.108$	$71.4 \pm 52.3$	$4.5 \pm 0.1$	$-3.50 \pm 0.78$	$-43.2 \pm 11.9$
pullulan(440k)	$41.6 \pm 0.2$	$0.234 \pm 0.065$	$84.9 \pm 21.9$	$3.7 \pm 0.1$	$-1.47 \pm 0.02$	$-14.3 \pm 0.3$

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May 16, 2012

Dear Dr. Michael Spencelayh:

We would like to submit our revised manuscript entitled "Temperature Dependence of Thermal Diffusion for Aqueous Solutions of Monosaccharide, Oligosaccharide, and Polysaccharide". The manuscript ID is CP-ART-04-2012-041183.

Our responses to reviewer's comments have been written in [blue](#) on the following pages.

We would appreciate it if you consider the suitability of our manuscript for a publication in PCCP.

Yours sincerely,  
Rio KITA

Reviewer(s)' Comments to Author:

Referee: 1

Comments to the Author

This paper reports on the temperature and molecular-weight dependencies of the Soret effect of polymers in aqueous solution. Part of the results on the temperature dependence have been reported in earlier articles by these groups, yet most of the data are novel.

The paper is rather well written and provides a good introduction. I recommend publication yet suggest that the authors consider the following remark:

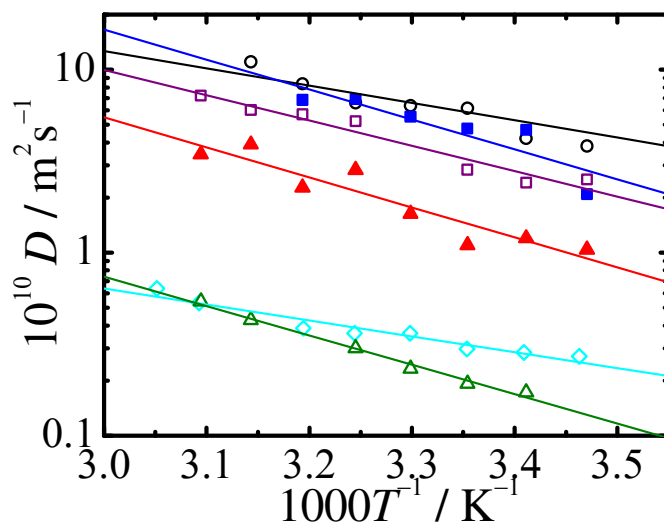
It is useful that in several figures, the authors compare the temperature dependence of the Einstein coefficient, the thermal diffusion coefficient, and the Soret coefficient. This presentation gives evidence for the existence of two independent temperature effects. The discussion of these curves, however, is a bit less satisfactory.

First of all, we would like to thank for the comments and suggestions by Referee 1.

According to the comments we added a discussion regarding to the temperature influence on the mutual diffusion, the thermal diffusion, and the Soret coefficient in Results and Discussion section.

The T-dependence of the Einstein coefficient is rather well understood in terms of Eyring's model for the dynamical viscosity. On the other hand, the Soret coefficient is independent of the viscosity; its temperature variation hints at a subtle property of thermal diffusion. These two effects are superposed in the temperature variation of  $DT=D \cdot ST$ .

We agree with Referee 1 that the mutual diffusion coefficient is well understood in comparison with the thermal diffusion that we have emphasized in the introduction. In the manuscript we have added a discussion about the temperature dependence of  $DT$ ,  $D$ , and  $ST$ . We checked the Eyring model for our measurements and found reasonable agreement.



Following the argumentation of the referee, he might suggest to combine the theoretical derived expression by Eyring and the empirical equation by Piazza in the following way

$$\begin{aligned}
 D_T &= D \cdot S_T \\
 D_T &= D_0 \exp(-E/T) \cdot S_T^\infty \left( 1 - \exp\left(\frac{T_{inv} - T}{T_0}\right) \right) \\
 &= D_0 \cdot S_T^\infty \left( \exp(-E/T) - \exp\left(\frac{T_{inv} - T}{T_0} - \frac{E}{T}\right) \right) \\
 &= K_{DS} \left( \exp(-E/T) - \exp\left(\frac{T_{inv} - T}{T_0} - \frac{E}{T}\right) \right)
 \end{aligned}$$

Using this expression would lead to four adjustable parameters and due to the weak temperature dependence it will not be possible to determine them all. Therefore, we limited our discussion Eq. 9, but we discuss in the text that such a approach can be considered.

Additionally, we added one figure where we discuss the effect of the viscosity based of the arguments of recent experimental results on DT as a function of the molecular weight (of polystyrene) as shown in the last figure of manuscript.

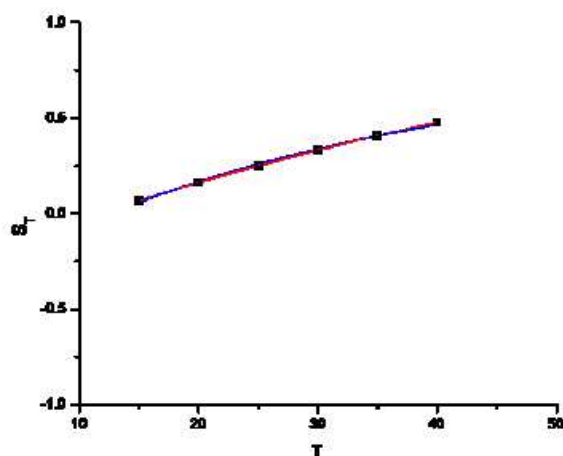
The fit of ST with Piazza's formula (4) highlights the importance of this law even if its physical meaning is not clear. One may suspect that it is related to the thermal expansion coefficient of water. In view of the above argument, the fit of DT with (9) is much less convincing. Alternatively the authors could fit the Einstein coefficient with Eyring's process,  $D = D_0 \exp(-E/T)$ , where E is an activation energy. I strongly suggest the authors discuss the T-dependence of D and DT according these lines.

It was confirmed that the mutual diffusion coefficient D of all samples studied in the report shows a linear relation when it is plotted against 1/T. The results are discussed in the manuscript. On the other hand, the thermal diffusion coefficient  $D_T$  follows not the Eyring's equation.  $D_T$  has negative values and changes sign with temperature, but even in the range of positive values of  $D_T$ , it does not follow an Arrhenius behavior.

Referee: 2

#### Comments to the Author

The authors present the intriguing finding of thermal diffusion in the binary systems of mono-, oligo-, and poly- saccharide in water. Specifically, they found a master curve exist for thermal diffusion coefficient, but not valid for Soret coefficient. The molecular weight dependence is also studied in this work. The conclusion is interesting and suitable for the readers of PCCP. However, I have questions for their fitting process. I cannot suggest a publication until I am convinced that their fitting results are reliable.



In fig 2, maltotriose is very different with glucose and maltohexaose although its MW is also low. When authors fit the data in fig 1 using eq. 4, do they leave all three parameters ( $T_{inv}$ ,  $S(\infty)$  and  $T_0$ ) free? If this is the case, I cannot trust the fitting results since those fittings are really not that sensitive. You can get very different fitting results even with slightly different data.

See above figure, red line I used the same parameters as authors used. For blue line, I used  $T_{inv}$  with 12.67,  $S(\infty)$  with 0.008,  $T_0$  with 31.49. See how close they are! I have no idea what is the error bar of  $ST$  in figure 1, but you can see two fitting lines are almost the same. Using my parameters, the  $A$  is around 9. Then maltotriose could have similar master curve as glucose and maltohexaose in figure 2, which is completely different with authors' results. If there are no restrictions of fitting parameters, I cannot be convinced by any fitting in this manuscript. If the error bars of  $ST$  are relatively large, then the fitting is more meaningless without restrictions.

We would like to thank for the comments of referee 2. As mentioned below we carried out some variations for fitting procedures and we think the revised manuscript became better due to the referee's comments.

We modified the top figure in Fig 1, so that the  $ST$  values of glucose and oligomers are easier to see in the graph. Now the inset shows all of data points of  $ST$  and the normal size figure shows the  $ST$  values of glucose and oligomers. So we exchanged inset and normal figure. Here, error bars have been added on data points of glucose. The error bars are very similar in the other systems, so we have left them out for clarity. As can be seen the size of error bars is within the symbol size.

We carried out the fitting of  $ST$  using Eq. (4) with several trial procedures as follows:

1. Nonlinear least square fit was tried with several sets of initial trial values.
2. We tried to use a constrained fit by fixing the  $T_0$  or  $T_{inv}$  at the value obtained in the other systems.
3. We tried some weighted fits with errors and an unweighted fit.
4. We tried to judge the relative deviation from the fit on figures to take into account a systematic deviation.

5. We obtained final fitting values with a chi-square judgment. We tried to find the fitting result where the chi-square value was around 1.

As the result of the fitting procedures, the parameters have changed slightly, but results are the same principally. Also we modified table by adding the error values of the fitted parameters as shown in Table 1.

As pointed out by the referee the fitting procedure is somehow controversial, especially for the data like the glucose and the maltotriose as in this study. This point has been added to Results and Discussion.

There are also some other problems. The experimental part is too simple. Authors used 5g/L solution in their previous paper, this paper used 10 g/L. Any concentration dependence? Some typos

Regarding to the experimental parts, the details of experimental method have been already published and which are cited, then we do not want to repeat experimental details. The concentration measured in this study is 10g/L. The referred data of high molecular weight polysaccharides (dextran and pullulan-440k) were measured at 5g/L. In the concentration range, we have studied several concentrations in dextran (Biomacromolecules 7 , 435 (2006)), PEO (JCP 118, 8073 (2003)), and PNIPAM (JCP 121, 9140 (2004)), but did not see a large effect on the thermal diffusion behavior. Probably below 10 % not much is happening. This point is added in the text in Experimental section and Results and Discussion section.

We did our best to eliminate typos.



The thermal diffusion coefficients of saccharides in water fall on a single curve when they are plotted as a function of  $\Delta T$  ( $=T_{\text{inv}}-T$ ).

